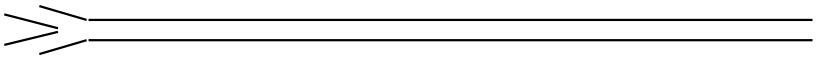
Appendix A



Acronyms and Symbols

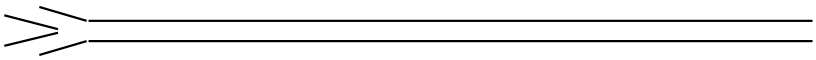
Acronyms

A	ACS	American Chemical Society
	AOAC	AOAC-International; formerly the Association of Official Analytical Chemists
	AOX	adsorbable organic halides
	APHA	American Public Health Association
	ASTM	formerly the American Society for Testing and Materials
	ATP	alternate test procedure
	AWWA	American Water Works Association
B	BAC	Biological Advisory Committee
	BOD	biochemical oxygen demand
C	CAS	Chemical Abstract Services
	CF	calibration factor
	CFR	*Code of Federal Regulations*
	CVAA	Cold Vapor Atomic Absorption
	CWA	Clean Water Act
D	DEEMS	*Department of Energy Environmental Management Electronic Data Deliverable Master Specification*
E	EAD	Engineering and Analysis Division
	ECD	electron capture detector
	ELCD	electrolytic conductivity detector
	EMMC	Environmental Monitoring Management Council
	EPA	Environmental Protection Agency
F	FID	flame ionization detector
	FLAA	flame atomic absorption
	FOIA	Freedom of Information Act
	FR	*Federal Register*
G	GC	gas chromatography
	GC/HRMS	gas chromatography/high resolution mass spectrometry
	GC/LRMS	gas chromatography/low resolution mass spectrometry
	GC/MS	gas chromatography/mass spectrometry
	GFAA	graphite furnace atomic absorption
H	HPLC	high performance liquid chromatography
	HRGC	high resolution gas chromatography
	HRMS	high resolution mass spectrometry
I	ICP/AES	inductively coupled plasma/atomic emission spectroscopy
	ICP/MS	inductively coupled plasma/mass spectrometry

	IPR	initial precision and recovery
	IR	infra-red spectroscopy
J K	JAOAC	*Journal of AOAC - International*
L	LOQ	limit of quantitation
M	MCAWW	*Methods for Chemical Analysis of Water and Waste*
	MCL	maximum contaminant level
	MDL	method detection limit
	ML	minimum level
	MS	matrix spike
	MSD	matrix spike duplicate
	MSDS	material safety data sheet
N	NCASI	National Council of the Paper Industry for Air and Stream Improvement, Inc.
	NELAC	National Environmental Laboratory Accreditation Committee
	NERL-Ci	National Exposure Research Laboratory - Cincinnati
	NIST	National Institute of Standards and Technology
	NPD	nitrogen phosphorous detector
	NPDES	National Pollutant Discharge Elimination System
	NPDWR	National Primary Drinking Water Regulations
	NTTAA	National Technology Transfer and Advancement Act of 1995
O	OECA	Office of Enforcement and Compliance Assurance
	OFR	Office of Federal Register
	OGC	Office of General Counsel
	OGWDW	Office of Ground Water and Drinking Water
	OPR	ongoing precision and recovery
	ORD	Office of Research and Development
	OST	Office of Science and Technology
	OSW	Office of Solid Waste
	OW	Office of Water
P	PAH	polynuclear aromatic hydrocarbon
	PID	photoionization detector
	POTW	publicly owned treatment works
	PWS	public water system
Q	QA	quality assurance
	QC	quality control
R	RF	response factor
	RPD	relative percent difference
	RR	relative response

	RRT	relative retention time
	RSD	relative standard deviation
	RT	retention time
S	SDWA	Safe Drinking Water Act
	SEM	standard error of the mean
	SRM	Standard Reference Material
T	TDS	total dissolved solids
	TOC	total organic carbon
	TSS	total suspended solids
U V	USGS	U.S. Geological Survey
W X Y Z	WEF	Water Environment Federation
	WET	whole effluent toxicity

Appendix B



Glossary

Glossary

	40 *CFR* part 136	Title 40, part 136 of the *Code of Federal Regulations*. This part specifies EPA's test procedures for the analysis of pollutants regulated under the Clean Water Act.
	40 *CFR* part 141	Title 40, part 141 of the *Code of Federal Regulations*. This part specifies EPA's National Primary Drinking Water Regulations pursuant to the Safe Drinking Water Act; Subpart C of 40 *CFR* part 141 lists analytical methods required for monitoring under the Act.
	95% confidence interval	A statistical level indicating a 95 % probability that the parameter variable is enclosed within the given data interval.
A	accuracy	The degree of agreement between an observed value and an accepted reference value. Accuracy includes random error (precision) and systematic error (bias) that are caused by sampling and analysis.
	aliquot	A representative portion of a sample. (QAMS)
	analysis of variance	A study of the effect of a set of qualitative variables on a quantitative response variable, based on a decomposition of the variance of the response variable.
	analyte	The substance, a property of which is to be measured by an analysis. (QAMS)
	analyte of concern	An analyte designated by EPA to adversely affect or have the potential to adversely affect human health, the environment, aesthetics, or the senses. Analytes of concern are listed in approved methods.
	analysis	The determination of the nature or proportion of one or more constituents of a sample.
	approved method	A testing procedure (analytical method) promulgated at 40 *CFR* parts 136, 141, 405-500, and other parts of the CFR that support EPA's water programs.
	average percent recovery	The average of the recovery, expressed as percent. See "recovery."
B	bias	A systematic or persistent distortion of a measurement process that deprives the result of representativeness; i.e.,

		the expected sample measurement is different than the sample's true value. A data quality indicator. (QAMS)
	blank	See "method blank."
C	calibration	The process of establishing the relationship between the concentration or amount of material introduced into an instrument or measurement process and the output signal.
	calibration factor	The quotient of instrument response and concentration of a standard obtained during instrument calibration. Unknown sample concentrations are determined by multiplying the determined calibration factor by the measured instrument response.
	calibration linearity	The degree to which calibration points lie along a straight line.
	calibration verification	Means of establishing that the instrument performance remains within pre-established limits.
	Code of Federal Regulations	A codification of the general and permanent rules published in the *Federal Register* by the Executive departments and agencies of the Federal Government.
	compliance	A state of meeting all requirements.
	confidence interval	The numerical interval constructed around a point estimated of a population parameter, combined with a probability statement (the confidence coefficient) linking it to the population's true parameter value. If the same confidence interval construction technique and assumptions are used to calculate future intervals, they will include the unknown population parameter with the same specified probability. (EMMC)
	contract laboratory	Private, academic, or commercial laboratory under contract to EPA or other organization to perform testing.
	correlation coefficient	A number between -1 and 1 that indicates the degree of linearity between two variables or sets of numbers. The closer to -1 or +1, the stronger the linear relationship between the two (i.e., the better the correlation.) Values close to zero suggest no correlation between the variables. The most common correlation coefficient is the product-

		moment, a measure of the degree of linear relationship between two variables. (EMMC)
D	data quality objective	Qualitative and/or quantitative statement of the overall level of uncertainty that a decision-maker is willing to accept in results or decisions derived from environmental data. Data quality objectives provide the statistical framework for planning and managing environmental data operations consistent with the data user's needs. (EMMC)
	determinative technique	The physical and/or chemical process by which measurement of the identity and concentration of an analyte is made. For most methods, the determinative technique consists of an instrumental measurement.
	digestion	Solubilization of the analytes in sample by destruction of the sample matrix. Most commonly performed in the determination of metals.
	direct final promulgation	The promulgation of a final rule in the CFR without first being proposed. This procedure is used when the rules are not expected to generate significant negative comments.
	discharge	Generally, any spilling, leaking, pumping, pouring, emitting, emptying or dumping (40 *CFR* 109.2; 110.1; 116.3); also, see "discharge of a pollutant" (40 *CFR* 122.2); the medium that is spilled, leaked, pumped, poured, emitted, emptied, or dumped.
	discharge of pollutant	Any addition of any pollutant or combination of pollutants to (1) waters of the U.S. from any point source or (2) to the waters of the contiguous zone or the ocean from any point source other than a vessel or other floating craft which is being used as a means of transportation (40 *CFR* 122.2; 401.11)
	distillation	The process of heating a mixture to separate the more volatile from the less volatile parts, then cooling and condensing the resulting vapor so as to produce a more nearly pure or refined substance: nonvolatile impurities remain in the residue. (Webster's)
E	effluent	A medium that flows out of a point source, e.g., the discharge from a sewage treatment plant.
	explicit flexibility	Modifications that are explicitly allowed in an approved method.

	extraction	The process of selectively transferring a substance from one phase to another or from one liquid to another with differing characteristics, then separating the phases or liquids to isolate the substance; e.g., transferring organic analytes from an aqueous liquid to an organic liquid.
	extreme rank sum test	A test to determine if laboratory performance significantly deviates from that of another lab.
F	facility	A plant or group of plants within a single location that is regulated under a single National Pollutant Discharge Elimination System (NPDES) permit and/or SDWA. A single facility may have multiple water supplies, discharges, waste streams, or other environmental media that are subject to compliance monitoring. For example, a single facility within the Pulp, Paper, and Paperboard industrial category may have a direct discharge, an indirect discharge, and an in-process waste stream that are all subject to compliance monitoring.
	Federal Register	A daily publication that provides a uniform system for publishing Presidential and Federal agency documents. Documents published in the *Federal Register* make changes to the CFR to keep the CFR current. (OFR)
	front-end technique	Any technique in the analytical process that precedes the determinative technique, including all procedures, equipment, solvents, etc. that are used in the preparation and cleanup of a sample for analysis. Front-end techniques does not include conditions and/or procedures for the collection, preservation, shipment, and storage of the sample.
G **H**	Guidelines and Format	The document titled *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 and 141*; available from the National Technical Information Service (NTIS), U.S. Department of Commerce, Springfield, Virginia, 22161 (703-487-4600) as NTIS publication PB96-210448.
I	incorporation by reference	A means for allowing the Federal agencies to comply with the requirement to publish regulations in the *Federal Register* by referring to materials already published elsewhere. The material incorporated by reference has the force and effect of law. (OFR)

industrial category	A category listed in 40 *CFR* parts 405-503.
industrial subcategory	A subcategory defined at 40 *CFR* parts 405-503.
initial precision and recovery	The analysis of a minimum of four spiked replicate reference matrix samples under the same conditions as will be used for analysis of environmental samples. The IPR is used to demonstrate that a laboratory is able to produce reliable results with the method prior to analysis of environmental samples.
interference	A positive or negative effect on a measurement caused by a substance other than the one being investigated. (QAD)
interlaboratory	Occurring in multiple laboratories.
interlaboratory method	A study conducted according to the principles outlined in Guidelines for Collaborative Study Procedures to Validate Characteristics of a Method of Analysis; JAOAC 78 No. 5, 1995; *Statistical Manual of the Association of Official Analytical Chemists*, W.J. Youden and E.H. Steiner, 1975 (published by AOAC-International, 481 N. Frederick St., Gaithersburg, MD 20877-2417; 301-924-7077); *Use of Statistics to Develop and Evaluate Analytical Methods* (published by AOAC-International); ASTM Standard D-2777 (published by ASTM, 100 Barr Harbour Drive, West Conshocken, PA 19428-2959; 610-832-9500); or other well-established and documented principles for interlaboratory method validation studies.
intralaboratory	Occurring within a single laboratory.

J K L

labeled compound	An isotopically labeled form of the native compound.
labeled compound recovery	The percentage of the labeled compound recovered. See "recovery."
laboratory	A person that owns or leases a stationary or mobile facility in which a sample is tested for an analyte.
log-normal	A distribution of a random variable X such that the natural logarithm of X is normally distributed.

M

matrix	The component or substrate that contains the analytes of interest. (NELAC QS)
matrix effect	Variability in the analytical performance of a method that can be attributed to the type of sample analyzed.
matrix spike	A sample prepared by adding a known mass of target analyte to a specified amount of a sample matrix for which an independent estimate of target analyte concentration is available. A matrix spike is used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)
matrix spike duplicate	A replicate of the matrix spike to test precision. The MS/MSD are used in combination to test the precision of an analysis. (QAMS)
matrix type	A sample medium with common characteristics across a given industrial category or subcategory. For example, C-stage effluents from chlorine bleach mills, effluent from the continuous casting subcategory of the iron and steel industrial category, POTW sludge, and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory are each a matrix type. For the purposes of this initiative all drinking waters constitute a single matrix type.
measurement quality objective	Critical level which, if exceeded, is considered to append additional, and possibly unacceptable, measurement uncertainty to the corresponding data.
medium	The physical phase of a sample matrix. Air, water, soil are sample media.
method	A body of procedures and techniques for performing a task (e.g. sampling, characterization, quantitation) systematically presented in the order in which they are to be executed. (QAMS)
method blank	A clean sample (absent of the analytes of interest and interferences) processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedure. (QAMS)

method-defined analyte	An analyte without a specific, known composition where the analytical result depends totally on the measurement procedure.
method detection limit	The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. For an MDL study, it is essential that all sample processing steps of the analytical method be included.

[The MDL results from estimating a method's sensitivity at the two lowest levels, zero concentration, and the lowest concentration that the method is capable of distinguishing from zero with a 99% probability.]

method modification	A change made to an approved method. The change may be to a front-end technique or to the determinative technique.
method validation	A process by which a laboratory or vendor establishes the performance of a new method or substantiates the performance of a method modification.
Methods and Criteria	The document titled: *Analysis of Pollutants in Municipal Water and Industrial Wastewater: Test Procedures and Quality Control Acceptance Criteria*; available from the National Technical Information Service (NTIS), U.S. Department of Commerce, Springfield, Virginia, 22161 (703-487-4600) as NTIS publication PB96-210463, and incorporated by reference into this part.
mid-point response factor	The response factor at the concentration at which calibration is verified.
minimum level	The lowest concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point for an analyte. It is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been employed. (40 *CFR* 132.2)
modified method	An approved method that has been modified to change a front-end technique or the determinative technique, either using method-specified flexibility or expanded flexibility allowed under streamlining

N

navigable waters — All waters of the United States, including the territorial seas. (40 *CFR* 110.1)

new method — A method that employs a determinative technique for an analyte of concern that differs from determinative techniques employed for that analyte in methods previously approved at 40 *CFR* part 136 or 141. In addition, it must (1) employ a determinative technique that is more sensitive and/or selective (specific) than the determinative techniques in all methods previously approved for the analyte, (2) contain the standardized QC elements detailed in Chapter 3 of the Streamlining Guide, (3) specify, for all standardized QC elements, QC acceptance criteria that have been developed in accordance with the requirements described in Chapter 3 of the Streamlining Guide, and (4) be documented in accordance with the requirements detailed in the *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141* or other standard format.

O

other approved methods — Promulgated methods that are not designated as a reference method, but continue to carry the same regulatory status.

P

percent recovery — 100 times the recovery.

phthalate — An ester of phthalic acid containing the radical $C_6H_4(COO)_2$=; used for buffers, for standard solutions, and in vacuum pumps. Certain phthalate esters are Priority Pollutants.

precision — The degree to which a set of observations or measurements of the same property, usually obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms. (QAMS)

[The precision obtainable from an environmental measurement method may be estimated from replicate analyses of subsamples taken from the same (homogenous) sample. Generally speaking, the more carefully one executes the various steps of a method and controls the variables affecting the method's capability, the more precise will be the results. The use of a nonhomogeneous sample will compound the precision estimate with the sample variability.]

preparation — Processing performed on a sample prior to analysis, e.g. extraction, concentration, cleanup, etc.

	procedures	A set of systematic instructions for performing an activity. (QAD)
	promulgated method	A method that has been published or incorporated by reference into 40 *CFR* parts 136, 141, 405-500, or other parts that support EPA's water programs.
	promulgation	Publication of a final rule in the FR.
	public water system (PWS)	A system for the provision to the public of piped water for human consumption, if such system has at least fifteen service connections or regularly serves an average of at least twenty-five individuals daily at least 60 days out of the year. Such term includes (1) any collection, treatment, storage, and distribution facilities under control of the operator of such system and used primarily in connection with such system, and (2) any collection or pretreatment storage facilities not under such control which are used primarily in connection with such system. A public water system is either a “community water system” or a “noncommunity water system.”
Q	quality assurance	An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)
	quality control	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical. (QAMS)
	QC acceptance criteria	Performance specifications developed from validation data and used to control the limits within which an analytical method is operated.
R	recovery	The total amount of the analyte found in the sample divided by the amount of the analyte added into the sample as a spike.
	reference method	A method that has been approved at 40 *CFR* part 136 or 141, contains (or is supplemented with) standardized quality control (QC) and QC acceptance criteria that define the required level of performance, and has been designated as a reference method in the tables appearing at 40 *CFR* part

		136 or 141. The reference method serves as a standard against which method modifications can be statistically compared.
	regulated entity	Permittees, PWSs, POTWs, and other entities responsible for compliance with provisions of the CWA or SDWA.
	relative response	The ratio of the response of an analyte relative to the response of a labeled compound.
	relative retention time	The chromatographic elution time relative to an isotopically labeled compound or internal standard.
	relative standard deviation	The standard deviation expressed as a percentage of the mean ($100\sigma/X$); i.e., the coefficient of variation.
	response factor	The inverse of the calibration factor. The slope of the line.
	responsible person/party	See “regulated entity.”
	retention time	Elution time specific to a given sample.
S	sample matrix	See "matrix."
	sample matrix effect validation	A test of the extent to which differences, if any, in method performance could be attributed to variability between samples obtained from different industrial matrices, facilities, or PWSs.
	sample medium	See "medium."
	screening method	A method that employs a determinative technique for an analyte of concern that differs from determinative techniques employed for that analyte in methods previously approved at 40 *CFR* part 136 or 141. In addition, it must (1) be demonstrated to produce a false negative probability of no more than one percent, (2) contain the standardized QC elements detailed in Chapter 3 of the Streamlining Guide, (3) specify, for all standardized QC elements, QC acceptance criteria that have been developed in accordance with the requirements described in Chapter 3 of the Streamlining Guide, and (4) be documented in accordance with the requirements detailed in the *Guidelines and Format*

	for Methods to be Proposed at 40 CFR Parts 136 or 141 or other standard format.
selectivity	The capability of a method or instrument to respond to an analyte in the presence of interferences.
sensitivity	The capability of a method or instrument to differentiate between different amounts or concentrations of an analyte.
spike	The process of adding a known amount of target analyte to a sample; used to determine the recovery efficiency of the method. (QAMS)
spike amount	A known mass of analyte added to a sample and used to determine the recovery of a method.
stakeholder	A party with a vested interest in a particular program. For EPA's water methods program, such parties include dischargers, permittees, analytical laboratories, vendors, method-developing organizations, and local, regional, state, and federal permitting and regulatory agencies.
standard deviation	The measure of the dispersion of observed values expressed as the positive square root of the sum of the squares of the difference between the individual values of a set and the arithmetic mean of the set, divided by one less than the number of values in the set.
standard error of the mean	The standard deviation of the sampling distribution of the mean; a measure of sampling error.
standardized quality control	Uniform performance testing procedures that ensure reliable results. The procedures can include calibration linearity, calibration verification, absolute and relative retention time precision, initial precision and recovery, ongoing precision and recovery, analysis of blanks, surrogate or labeled compound recovery, matrix spike and matrix spike duplicate recovery and precision, demonstration of method detection limits, and analysis of a reference sample.
straw man	A draft document proposed for the purpose of generating public interest, comments, and suggestions to possible changes without committing EPA to a course of action.

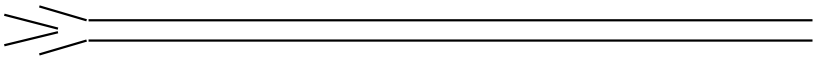
	streamlining	A process to improve the performance of a program while retaining the mechanisms to retain data quality (e.g., reducing costs, resources, or wastes).
	Streamlining Guide	The document titled: Guide to Method Flexibility and Approval of EPA Water Methods; available from the National Technical Information Service (NTIS), U.S. Department of Commerce, Springfield, Virginia, 22161 (703-487-4600) as NTIS publication PB96-210455 and incorporated by reference into this part.
	Student's *t* distribution	A type of sampling distribution for a random variable. A normal distribution divided by the square root of a chi-square distribution divided by its degrees of freedom.
	surrogate	A substance with properties that mimic the analyte of interest that is unlikely to be found in an environmental sample and that is added to the sample for quality control purposes. (QAMS)
	surrogate recovery	The recovery for a surrogate. See "recovery."
T	Tier 1	The application of a new or modified method in a single laboratory to one or more matrices. Method validation requirements are limited to single laboratory testing on the matrix type or matrix types of interest.
	Tier 2	The application of a new or modified method to samples from a single matrix type in a single industrial category or subcategory. Method validation requires an interlaboratory study on samples collected from a minimum of 3 separate facilities each in a minimum 3 laboratories to confirm method performance or to establish QC acceptance criteria for the method.
	Tier 3	The application of a new or modified method to all matrix types. Method validation requires an interlaboratory method validation study or a study of 9 matrix types in 9 laboratories to confirm method performance or to establish QC acceptance criteria for the method.
U V	variance	A measure of the dispersion of a set of values. The sum of the squares of the difference between the individual values of a set and the arithmetic mean of the set, divided by one

	less than the number of values in the set. (The square of the sample standard deviation.) (QAMS)
validate	Method validation

The above definitions are referenced to the following organizations:

EMMC	Environmental Monitoring Management Council
NELAC QS	National Environmental Laboratory Accreditation Conference, Quality Systems
OFR	Office of Federal Register
QAD	Quality Assurance Division, National Center for Environmental Research and Quality Assurance, Office of Research and Development, USEPA
QAMS	Quality Assurance Management Staff

Appendix C



Current Method Flexibility

This chapter provides a summary report of stakeholder inquiries and EPA responses concerning the method flexibility allowed in the current 40 CFR 136 Appendix A analytical methods. These correspondences, generated in 1994 and 1995, were one impetus for undertaking the initiative to streamline the method approval process and method flexibility in the programs regulated by the Office of Water.

The narrow range of the raised issues reflects the limited flexibility that is currently allowed. The responses indicate the incremental approach that has been historically followed to improve test procedures. This appendix is provided to facilitate a comparison between the proposed and existing method flexibility.

ISSUE # 1 - CRITERIA FOR DETERMINING ACCEPTABLE METHOD MODIFICATIONS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
1.5	603	1.4
	608,625	1.5
8.1.2	603,608,625	8.1.2
EPA 821-B-93-001	603,608,625	EPA 821-B-93-001

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 11.1) to improve the separations or lower cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

EPA 821-B-93-001 "Guidance On Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", page 10, Flexibility in Analytical Methods: "The analyst is permitted to 'improve separations or lower the costs of analyses' provided that the results obtained are not less precise and accurate than the results obtained using the unmodified method".

Does this impact those areas in the method where the Agency has used words like "suggested", "should", or "recommended"?

Response: Yes.

Can changes be made to lower the cost of analyses, even if they are not specifically permitted in the method, so long as the accuracy and precision guidelines in the method can be met?

Response - No. Some method changes, such as substituting a flame ionization detector for a mass spectrometer in Method 624, constitute a new method and need to be brought to the permitting authority for a ruling. On the other hand, some areas of method flexibility, such as those discussed in this communication, have been reviewed by the Agency and judged to be reasonable in view of advances in measurement technology.

ISSUE # 2 - CALIBRATION VERIFICATION

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.4	603	7.5
	608	7.4
	625	7.3

7.4 The working calibration curve or RF must be verified on each working day by the measurement of a QC Check Sample.

Our interpretation of "working day" is every 24 hours. Is that acceptable?

Response: No. A working day for most people is 8 hours. Some methods specify 12 hours. Either is acceptable so long as calibration is verified. If calibration is not verified, samples analyzed during the previous "working day" must be inspected for a possible adverse effects. If instrument performance is degraded during the previous "working day," calibration must be verified or the instrument must be recalibrated, and the samples reanalyzed.

ISSUE # 3 - REQUIRED FREQUENCY OF MATRIX SPIKES

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.1.4	603,608,625	8.1.4
EPA 821-B-93-001	603,608,625	EPA 821-B-93-001

8.1.4 The laboratory must, on an on going basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

This requirement, when applied to a laboratory dedicated to a single discharge or a single set of discharges, is straightforward. Its application to commercial laboratories that analyze a wide range of discharge samples from many different facilities each month can be confusing. It could be interpreted to mean that a commercial lab that analyzes less than 20 samples per month (10 for Methods 603 and 608) from any one sampling site must spike a sample from that site at least once a month (regardless of how many spikes have been performed for other sampling sites). This could effectively mean that every sample analyzed for every discharge client will need to be spiked. This would greatly increase the cost of analysis to the regulated community. Alternatively, it could be interpreted to require that a commercial lab spike 5% (10% for Methods 603 and 608) of its total sample volume unless it analyzes less than 20 discharge samples per month (10 for Methods 603 and 608), in which case it must spike at least one sample per month.

Which interpretation is correct?

Response: Neither. The hierarchy of requirements are:

(1) The laboratory must analyze one spiked wastewater sample per month per method used in that period.

(2) The laboratory must analyze at least one spiked sample from each sample site.

(3) If the laboratory analyzes more than 20 samples from a site, at least 5% of the samples must be spiked.

Two examples to illustrate: if, using Method 604, laboratory A contracts to analyze one sample per week from a site over one year, and analyzes a total of 20 samples per month by Method 604 from this and other sites, three spiked samples from the site must be analyzed during the year. The laboratory may choose which sample to spike among the first twenty, the second twenty, and the last 12-20. If, using Method 604, laboratory B contracts to analyze one sample per quarter for a year, and analyzes a total of 20 samples by Method 604 from this and other sites in the same month that the sample is analyzed, the laboratory must spike one of the four samples. If the laboratories in these two examples analyzed no other samples with Method 604 during the year, laboratory A would spike 12 samples out of 52 and laboratory B would spike 4 of 4.

ISSUE # 4 - ONGOING METHOD ACCURACY DOCUMENTATION REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.6	603,608,625	8.5

8.6 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of 5 spiked wastewater samples as in section 8.3, calculate the average percent recovery and the standard deviation of the percent recovery... Update the accuracy assessment for each parameter (on) a regular basis (e.g. after each 5 to 10 new accuracy measurements).

Normally we focus our efforts on meeting the ongoing method QC criteria and the initial demonstration of accuracy and precision. We maintain the data necessary to calculate the accuracy assessment if it were ever requested. Is this acceptable?

Response: Yes.

ISSUE # 5 - INTERNAL STANDARD COMPOUNDS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.3	625	7.2

7.3 Internal standard calibration procedure--To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 3.

Are internal standards not in Table 3 (Table 8 for Method 625) acceptable? For instance, would the 524.2 or 8240 internal standards be acceptable for use in Method 624? Minimizing the number of internal standard solutions that the lab must maintain leads to substantial cost savings that are subsequently passed on to the regulated community.

Response: Alternate internal standards are acceptable provided that method performance is not degraded and the reason is justified and documented.

ISSUE # 6 - QUALITATIVE IDENTIFICATION REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
12.1.3	625	14.1.3

12.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within +/- 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

When setting up the GC/MS method, if the laboratory sets the limits in the software to 20%, there is a significant risk of false negatives due to coeluting compounds interfering with the ions of the target analytes. However, if the limits are broadened to minimize the chance of false negatives, there is no efficient means by which to measure this percentage. We believe that setting the ion ratio in the software large enough to guard against the possibility of false negatives (40%) and then visually inspecting the spectrum relative to the reference spectrum is within the flexibility allowed by the method. Does the Agency agree?

Response: Yes. The software should be set up to force false positives. The analyst must then determine which of the positives is false.

Section 12.1 (14.1 for Method 625) states that one primary and at least two secondary ions are to be used for quantitation. Tables 3 and 4 (Tables 4 and 5 for Method 625) list primary and secondary ions for the various analytes involved, but do not always list two secondary ions. Can the analyst use professional judgement to drop or add characteristic ions to account for interferences and other analytical problems?

Response: The analyst may choose alternate m/z's provided that the reason is justified and documented.

ISSUE # 7 - SURROGATE COMPOUND RECOVERY REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.5	625	8.6

8.5 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solutions as described in Section 11.4, and calculate the percent recovery of each surrogate compound.

All samples must be spiked with surrogate. No criteria are given. Can optional surrogate criteria be developed using statistical techniques or by using the surrogate limits given in EPA method 8260 (8270 for Method 625)?

Response: Optional surrogate QC criteria can be used.

ISSUE # 8 - REQUIRED CONCENTRATION OF MATRIX SPIKES

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
8.3.1	603,625	8.3.1

8.3.1 The concentration of the spike in the sample should be determined as follows:

> *8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*
>
> *8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*

Quite often the commercial laboratory is not aware that a sample is being tested for regulatory compliance or what the regulatory limit might be. In addition, it is often impractical and expensive to determine background levels before spiking and to vary spiking levels. A single spiking protocol at an acceptable concentration level results in greater efficiencies and a lower cost to the regulated community. Is it acceptable to spike at 20 ug/L (50 ug/L for Method 603, 100 ug/L for Method 625)?

Response: Yes, it is acceptable to alter the concentration of the spike so long as the concentration is (a) greater than the background concentration and (b) less than or equal to the regulatory compliance level.

ISSUE # 9 - ACCEPTABLE TRAP MATERIALS AND DIMENSIONS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.2.2	603	5.2.2
11.1	603	10.1

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 8.3.2),15 cm of 2,6-dyphenylene oxide polymer (Section 6.3.1). and 8 cm of silica gel (Section 8.3.3). The minimum specifications for the trap are illustrated in Figure 2.

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

Is the use of newer traps, having different dimensions and packing material with improved (decreased) retention of water and better desorption characteristics, considered "other chromatographic conditions" per Section 11.1 (Section 10.1 for Method 603) and thereby acceptable, so long as the requirements of Section 8.2 are met?

Response: Yes. The Agency has agreed that extension of method flexibility to include trap materials and conditions is appropriate.

ISSUE # 10 - ACCEPTABILITY OF CAPILLARY COLUMNS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.3.2	603	5.4.1
8.1.2	603	8.1.2
11.1	603	10.1

5.3.2 Column--6 ft long x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 11.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met. EPA 821-B-93-001 "Guidance On Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", page 10, Flexibility in Analytical Methods: "For example,

the analyst is allowed to use professional judgement in selecting packed or open tubular columns, operating temperature programs, carrier gas or solvent flow rates, and detectors".

We believe the use of capillary columns is within the flexibility allowed in sections 8.1.2 and 11.1 (10.1 for Method 603). Does the Agency agree?

Response: Yes. The Agency agrees that extension of method flexibility to include capillary columns is appropriate. Of course, a hardware upgrade may be required to handle the sharper peaks produced by capillary columns.

ISSUE # 11 - TRAP CONDITIONING REQUIREMENTS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.1	603	7.1

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180-C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

If the laboratory can adequately condition a trap in less time than "overnight", is this acceptable? For example, if a sample foams and the trap must be replaced, if the trap is conditioned during the day and analysis of a blank demonstrates that the system is clean, can analyses proceed?

Response: Yes.

ISSUE # 12 - PREPARATION OF CALIBRATION STANDARDS

The following citations are from Method 624. Identical or similar requirements are included in other Methods as follows:

METHOD 624 SECTION	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
7.3.1	603	7.3.1

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 uL of one or more secondary dilution standards to 50, 250, or 500 mL of reagent water. A 25 uL syringe with a 0.006 in. ID needle should be used for this operation. One of the calibration standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples

or should define the working range of the GC/MS system. These aqueous standards can be stored up to 24 h. if held in sealed vials with zero headspace as described in Section 9.2. If not so stored, they must be discarded after 1 h.

First, are syringes of other internal diameters acceptable?

Response: Yes.

Second, from this paragraph it would seem that the Agency wants to hold the volume of the intermediate standard pipetted constant and vary the size of the volumetrics. In other words, if we have to add 20 uL of intermediate solution and we only have three final volumes to chose from, there are only three possible concentrations we can make from our intermediate solution. Would it be acceptable to vary the amount of intermediate solution added or chose a different final volume when preparing these standards?

Response: Yes. The objective is to calibrate the instrument; the details may be varied.

ISSUE #13 - REQUIRED MASS ACQUISITION RANGE

This issue relates solely to Method 624.

5.3.3 Mass spectrometer--Capable of scanning from 20 to 280 amu every 7 s or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet. This paragraph defines the necessary scan speed for the mass spec to be from 20 to 280 in seven seconds or less. Does it also require that the scan range 20 to 280 be used for data acquisition? With this scan range, methanol would be the predominate peak in the total ion chromatogram. We believe that scanning from 33 to 280 is acceptable. This would still bracket all the characteristic ions of the analytes of interest presented in the method and exclude methanol. Does the Agency agree?

Response: No. Scanning from m/z 20 is required in order to rigorously identify acrolein and acrylonitrile, should they be present. If there is concern about the display of the total resolved ion chromatogram, the data can be displayed from m/z 45 upward and the m/z's resulting from air (nitrogen, oxygen, argon, CO_2) and methanol will not be visible.

ISSUE # 14 - SURROGATE COMPOUNDS, PREPARATION AND FINAL CONCENTRATIONS

This issue relates solely to Method 624.

6.7 Surrogate standard spiking solution-- Select a minimum of three surrogate compounds from Table 3. Prepare stock standard solutions for each surrogate standard in methanol as described in Section 6.5. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 15 ug/mL in water. Store the solutions at 4-C in Teflon-sealed glass containers with a minimum of

headspace. The solutions should be checked frequently for stability. The addition of 10 uL of this solution to 5 mL of sample or standard is equivalent to a concentration of 30 ug/L of each surrogate standard.

TABLE 3. SUGGESTED SURROGATE AND INTERNAL STANDARDS

Compound	*Retention time (min)[a]*	*Primary m/z*	*Secondary m/z's*
Benzene d-6	*17.0*	*84*	
4-Bromofluorobenzene	*28.3*	*95*	*174,176*
1,2-Dichloroethane d-4	*12.1*	*102*	
1,4-Difluorobenzene	*19.6*	*114*	*63,88*
Ethylbenzene d-5	*26.4*	*111*	
Ethylbenzene d-10	*26.4*	*98*	
Fluorobenzene	*18.4*	*96*	*70*
Pentafluorobenzene	*23.5*	*168*	
Bromochloromethane	*9.3*	*128*	*49,130,51*
2-Bromo-1-chloropropane	*19.2*	*77*	*79,156*
1,4-Dichlorobutane	*25.8*	*55*	*90,92*

(a)For chromatographic conditions, see Table 1.

Since Table 3 gives "Suggested Surrogate and Internal Standards", may alternative surrogates be utilized, such as those used in 524.2 or 8240, or is the laboratory bound to those on this list? Minimizing the number of surrogate solutions that the lab must maintain results in substantial cost savings that can subsequently be passed on to the regulated community.

Response: Alternate surrogates may be used.

When preparing standard solutions can the concentrations and/or volumes of the surrogate solutions be changed? Can the final concentration of the surrogates in the samples be changed? This would facilitate the use of commercially prepared solutions thereby decreasing the cost of performing the analysis.

Response: Yes. Surrogate concentrations may be changed.

ISSUE # 15 - SURROGATE COMPOUND RECOVERY REQUIREMENTS

This issue relates solely to Method 624.

8.5 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 11.4, and calculate the percent recovery of each surrogate compound.

All samples must be spiked with surrogate. No criteria are given. Can optional surrogate criteria be developed using statistical techniques or by using the surrogate limits given in EPA method 8240?

Response: See issue #7.

ISSUE # 16 - ANALYSIS OF ACROLEIN AND ACRYLONITRILE BY METHOD 624

This issue relates solely to Method 624.

1.2 The method may be extended to screen samples for acrolein (STORET No. 34210, CAS No. 107-02-8) and acrylonitrile (STORET No. 34215, CAS No. 107-13-1), however, the preferred method for these two compounds in (sic) Method 603.

Table 1C - List Of Approved Test Procedures For Non-Pesticide Organic Compounds, footnote #4: Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. However, when they are known to be present the preferred method for these two compounds is method 603 or method 1624.

We believe that if Method Detection Limits (MDLs) are documented and if accuracy and precision criteria in method 603 for Acrolein and Acrylonitrile can be met using method 624, that Acrolein and Acrylonitrile can legitimately be reported (at or above reporting limits consistent with the documented MDLs) from a method 624 analysis. Does the Agency agree?

Response: Yes, provided that the performance criteria and MDLs in Method 603 can be met using Method 624.

ISSUE # 17 - SAMPLE PRESERVATION REQUIREMENTS

This issue relates solely to Method 624.

9.3 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. (3) Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1+1 HCl while stirring vigorously. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2.

This preservation protocol could be interpreted to require three different sample analyses (to permit 14 day hold times) to determine the full 624 list (one sample for acrolein and acrylonitrile, one for purgeable halocarbons, and one for purgeable aromatics).

Can the purgeable halocarbons be analyzed from an acidified sample with a pH <2? Can acrolein and acrylonitrile be analyzed from an acidified sample with a pH <2 or is there some other preservation routine that will allow for fewer analyses?

Response: EPA recommends acidification and refrigeration as the principle preservation procedures for purgeable organic compounds. If the holding time is to be extended to 14 days, a minimum of two samples will be required. The first for acrolein adjusted to pH 4-5 per footnote 9 to Table II of 40 CFR part 136; the other to pH <2 with HCl per footnote 10 of this table. If free chlorine is present, it must be reacted with sodium thiosulfate per Table II.

ISSUE # 18 - REQUIRED CONCENTRATION OF QC CHECK SAMPLE

This issue relates solely to Method 608.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations:

8.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; endrin, 10 ug/mL; any other single-component pesticide, 2 ug/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 ug/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.3.1 The concentration of the spike in the sample should be determined as follows:

> *8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*
>
> *8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.*
>
> *8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory*

concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

As we understand the method, 1 mL of the QC Check standard from section 8.2.1 is added to 1 L of sample to prepare a matrix spike. The same amount of QC Check standard would be added to 1 L of reagent water to prepare a QC Check Sample. The samples are then concentrated to a final volume of 10 mL. This would result in the following concentrations in the extracts:

PARAMETER	CONC. IN EXTRACT (ug/L)
Aldrin	200
a-BHC	200
b-BHC	200
d-BHC	200
g-BHC	200
Chlordane	5000
4,4-DDD	1000
4,4-DDE	200
4,4-DDT	1000
Dieldrin	200
Endosulfan I	200
Endosulfan II	1000
Endosulfan Sulfate	1000
Endrin	1000
Heptachlor	200
Heptachlor epoxide	200
Toxaphene	5000
PCB-1016	5000
PCB-1221	5000
PCB-1232	5000
PCB-1242	5000
PCB-1248	5000
PCB-1254	5000
PCB-1260	5000

In all cases except Toxaphene these concentrations are above the normal linear range of an ECD detector when set up to achieve method 608 detection limits. The following are the spike concentrations and upper calibration limits we currently use:

PARAMETER	CONC. IN EXTRACT (ug/L)	UPPER CAL. LIMIT (ug/L)
Aldrin	30	50
a-BHC	30	50
b-BHC	30	50
d-BHC	30	50
g-BHC	30	50
Chlordane	50	1000
4,4-DDD	60	100
4,4-DDE	60	100
4,4-DDT	60	100
Dieldrin	60	100
Endosulfan I	30	50
Endosulfan II	60	100
Endosulfan Sulfate	60	100
Endrin	60	100
Heptachlor	30	50
Heptachlor epoxide	30	50
Toxaphene	3000	5000
PCB-1016	500	1000
PCB-1221	500	1000
PCB-1232	500	1000
PCB-1242	500	1000
PCB-1248	500	1000
PCB-1254	500	1000
PCB-1260	500	1000

Are these spike concentrations acceptable?

Response: Yes, provided all method-specified QC criteria are met.

ISSUE # 19 - ACCEPTABLE SAMPLE EXTRACTION PROCEDURES

This issue relates solely to Method 608.

10.2 If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

Allowances are made for the use of techniques to overcome emulsion problems. We have found that the most effective technique for dealing with emulsions is the use of continuous liquid/liquid

extractors. This technique is not specifically mentioned here. Since wastewater samples routinely cause emulsion problems, is continuous extraction an acceptable technique to use with this method?

Response: Yes, provided the procedure is an adaptation of Method 608 (neutral sample pH, methylene chloride-based extraction solvent, extended contact time to assure extraction of analytes from solids) and all method-specified QC criteria are met.

ISSUE # 20 - QUANTITATION PEAK REQUIREMENTS

This issue relates solely to Method 608.

13.3 For multicomponent mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

Please clarify what is meant by the phrase "every identifiable peak". The chromatogram of PCB or multicomponent pesticides may contain over 100 peaks of various heights. Since many of the smaller peaks disappear from low concentration standards and samples, we normally use only the largest, most distinctive peaks for quantitation. This tends to keep responses more linear and provides more accurate results at the lower concentration levels. Quantitation using all peaks tends to skew results near the detection limits so that samples appear to be lower in concentration than they actually are. This phenomenon is caused because the smaller peaks, which were used to develop the response factors, are no longer detectable as part of the sample constituent.

Response: Use the largest number of peaks that will provide reliable quantitation of the compound. Five peaks minimum is suggested.

ISSUE #21 - ACCEPTABILITY OF COMBINING ACID AND BASE/NEUTRAL EXTRACTS PRIOR TO ANALYSIS

This issue relates solely to Method 625.

10.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

Section 10.6 starts with the phrase "For each fraction", and goes on to describe the setup of a K-D concentration apparatus. It also states that alternative concentration techniques can be used if the requirements in section 8.2 are met. We have found that the most efficient way to perform this step is by concentrating the BN and A fractions together into one extract. This results in both an improvement in recoveries and lower costs to the regulated community.

The increase in cost when the fractions are kept separate is dramatic because it carries throughout the entire lab. Twice the amount of glassware is needed. Twice the amount of prep labor is needed to

perform the concentration step. Instrument time is doubled. Twice the number of reports are generated. Data reduction is slowed.

Also, when the extracts are not combined there is a drop in the recoveries of the acid compounds. This is caused because even at a pH greater than 11 the acid compounds are partially extracted into the basic fraction. Once there, they are essentially lost to the analysis unless the fractions are later combined.

In the end, keeping the fractions separate results in no real increase in quality and a dramatic increase in cost. Good resolution can still be maintained when the extracts are combined and the method detection limits are still easily achievable. Is it acceptable to combine the BN and A fractions as long as the requirements in Section 8.2 and the method detection limits can be met?

Response: Yes and No. If the analytes can be reliably identified and quantified in each sample, the extracts may be combined. If, however, the identification and quantitation of any analyte is adversely affected by another analyte, a surrogate, or an interferant, the extracts must be analyzed separately. If there is ambiguity, the extracts must be analyzed separately.

ISSUE # 22 - CHARACTERISTIC ION REQUIREMENTS

This issue relates solely to Method 625.

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification

Section 14.1 states that one primary and at least two secondary ions are to be used for qualitative identification of all compounds. Can the analyst use professional judgement to drop or add characteristic ions to account for interferences and other analytical difficulties?

Response: Yes, provided the identification of the analyte is as reliable as it would be if the specified m/z's were used.

ISSUE # 23 - CHROMATOGRAPHIC RESOLUTION REQUIREMENTS

This issue relates solely to Method 625.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

What ramifications does this have on compliance monitoring where benzo(k)fluoranthene and benzo(b)fluoranthene need to be identified? Should these compounds be reported as

"Benzofluoranthenes"? Is there any flexibility for analyst interpretation regarding isomer identification?

Response: If the isomers cannot be differentiated, the concentration should be checked against the lowest regulatory concentration limit for the pair. In this instance, EPA recommends that a column that resolves the pair be used.

ISSUE # 24 - QUANTITATION OF 2,3,7,8-TCDD

This issue relates solely to Method 625.

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows...

Does the term "screen" imply that the method is non-quantitative for 2,3,7,8-TCDD? What should be reported when performing this screen, "D" versus "ND"?

Response: Screen means that if 2,3,7,8-TCDD is detected, the sample must be analyzed using an alternate method specifically designed for the determination of 2,3,7,8-TCDD. EPA recommends Method 1613 for this determination.

ISSUE # 25 - ALTERNATIVE CAPILLARY COLUMNS

The following citations are from Method 601. Identical or similar requirements are included in other Methods as follows:

METHOD 601 SECTIONS	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.3.1 5.3.2	602	5.3.1 5.3.2
	624	5.3.2

5.3.1 Column 1 - 6 ft long x 0.082 in ID stainless steel or glass, packed with 5% 1,2,3-1200 and 1.75% Bentone-34 on Supelcoport (100/120 mesh) or equivalent...

5.3.2 Column 2 - 8 ft long x 0.1 in ID stainless steel or glass, packed with 5% Tris(2-cyanoethoxy)propane on Chromo W-AW (60/80 mesh) or equivalent...

Recently, new types of chromatographic columns have been developed that clearly demonstrate an enhancement in the state-of the art. Can these chromatographic columns be used in Methods 601, 602 and 624?

Response: In response to numerous requests, on July 5, 1989, the Environmental Monitoring Systems Laboratory (EMSL-Ci, now called NERL-Ci) recommended approval of the newer chromatographic columns in Methods 601, 602, and 624 provided that the user demonstrates the achievement of performance criteria. The performance criteria include accuracy, precision, and method detection limit as outlined in section 8.2 of the method(s) and Appendix B of 40 CFR part 136. EMSL-Ci recommended that the laboratory document the performance criteria prior to initiating any NPDES analyses.

ISSUE # 26 - COMBINATION OF 601 AND 602 METHODS

The following citations are from Method 601. Identical or similar requirements are included in other Methods as follows:

METHOD 601 SECTIONS	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.3.3	602	5.3.3

5.3.3 Detector - Electrolytic conductivity or microcoulometric detector...

Can Methods 601 and 602 be combined with use of a photoionization detector in series with an electrolytic conductivity detector?

Response: In response to numerous requests, on July 5, 1989, the Environmental Monitoring Systems Laboratory (EMSL-Ci, now called NERL-Ci) recommended approval of the combination of Methods 601 and 602 with the use of a photoionization detector in series with an electrolytic conductivity detector provided that the user demonstrates the achievement of performance criteria. The performance criteria include accuracy, precision, and method detection limit as outlined in section 8.2 of the method(s) and Appendix B of 40 CFR part 136. EMSL-Ci recommended that the laboratory document the performance criteria prior to initiating any NPDES analyses.

ISSUE # 27 - ALTERNATIVE SORBENTS TRAPS

The following citations are from Method 601. Identical or similar requirements are included in other Methods as follows:

METHOD 601 SECTIONS	OTHER PERTINENT METHOD(s)	EQUIVALENT SECTION(s)
5.2.2	602	5.2.2.1
	624	5.2.2

5.2.2 ...The trap must be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.3), 7.7 cm of 2,6-diphenylene oxide polymer (Section 6.3.2), 7.7 cm of silica gel (Section 6.3.4), 7.7 cm of coconut charcoal (Section 6.3.1)...

Recently, new material have become available that appear to provide advantages over the sorbent traps specified in the methods. Can these be used in place of the specified sorbents traps?

Response: On November 7, 1994, EMSL-Ci accepted of the use of alternative sorbents provided the data acquired meets all quality control criteria described in Section 8 and provided the purge and desorption procedures specified in the method are not changed. The performance criteria include accuracy, precision, and method detection limit as outlined in section 8.2 of the method(s) and Appendix B of 40 CFR part 136. EMSL-Ci recommended that the laboratory document the performance criteria prior to initiating any NPDES analyses.

Although alternative adsorbents may be used, only some of the purging and desorption procedures can be adjusted. The purging and desorption procedures were designed to achieve 100% purging efficiency and recovery of the many regulated target analytes. The purge time and purge gas flow rate required to efficiently purge the target analytes from the water samples are largely independent of the sorbent trapping material. Decreasing the purging or desorption times or gas flows will have a negative impact on method precision and may increase adverse matrix effects. Therefore, purge time and purge gas flow rate may not be adjusted. Since many of the potential alternate sorbents may be thermally stable at temperatures higher than 180 °C, however, the alternate traps may be desorbed and baked out at higher temperatures than those described in the current method revisions. If higher temperatures are used, the analyst should monitor the data for analyte and trap decomposition.